

United States Patent [19]
Takahashi et al.

[11] **Patent Number:** **4,647,582**
[45] **Date of Patent:** **Mar. 3, 1987**

[54] **FUNGICIDAL ANILINE DERIVATIVES**

[75] **Inventors:** Junya Takahashi, Nishinomiya;
Toshiro Kato, Takarazuka; Hiroshi
Noguchi; Yukio Oguri, both of
Toyonaka; Shigeo Yamamoto, Ikeda;
Katsuzo Kamoshita, Osaka, all of
Japan

[73] **Assignee:** Sumitomo Chemical Company,
Limited, Osaka, Japan

[21] **Appl. No.:** 565,169

[22] **Filed:** Dec. 23, 1983

[30] **Foreign Application Priority Data**

Jan. 13, 1983 [GB] United Kingdom 8300813
Jan. 17, 1983 [GB] United Kingdom 8301146

[51] **Int. Cl.⁴** A01N 47/20; C07C 125/067

[52] **U.S. Cl.** 514/482; 514/485;
514/508; 514/521; 514/628; 558/389; 560/27;
560/29; 560/301; 564/211; 564/214

[58] **Field of Search** 560/24, 27, 29, 301;
424/300; 260/465 D, 455 A; 514/482, 485, 508,
521, 628; 558/389; 564/211, 214

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,781,327 12/1973 Teach 560/29
4,482,546 11/1984 Takahashi et al. 260/465 D

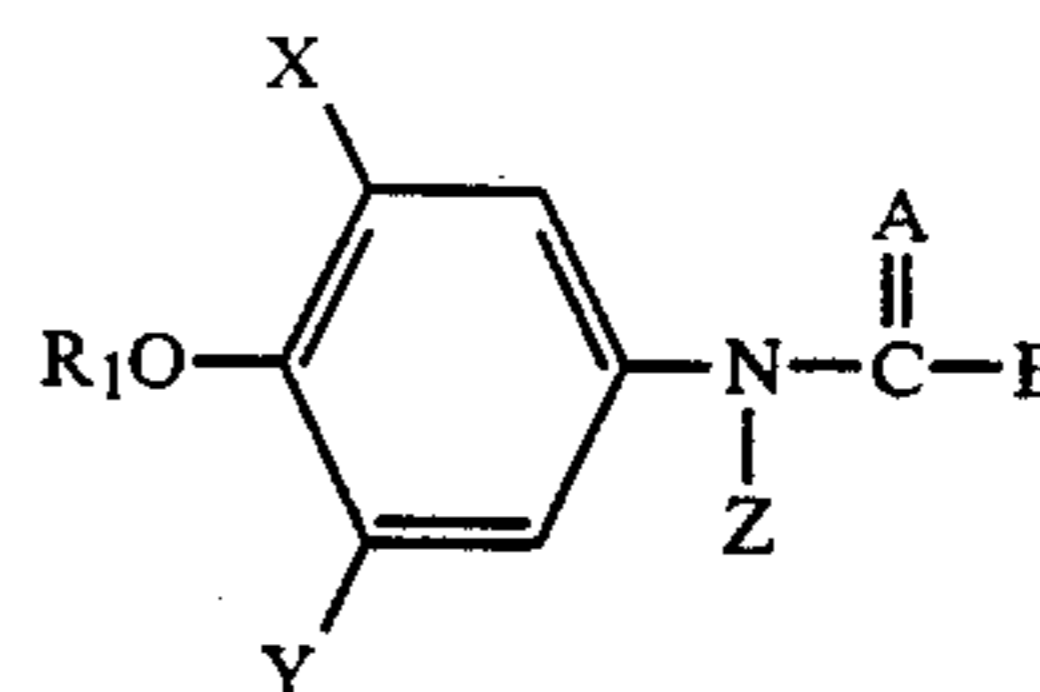
FOREIGN PATENT DOCUMENTS

0051871 5/1982 European Pat. Off. .

Primary Examiner—Dolph H. Torrence
Attorney, Agent, or Firm—Birch, Stewart, Kolasch &
Birch

[57] **ABSTRACT**

A compound of the formula:



useful as a fungicidal agent against phytopathogenic
fungi, and particularly against strains resistant to benz-
imidazole, thiophanate and/or cyclic imide fungicides.

3 Claims, No Drawings

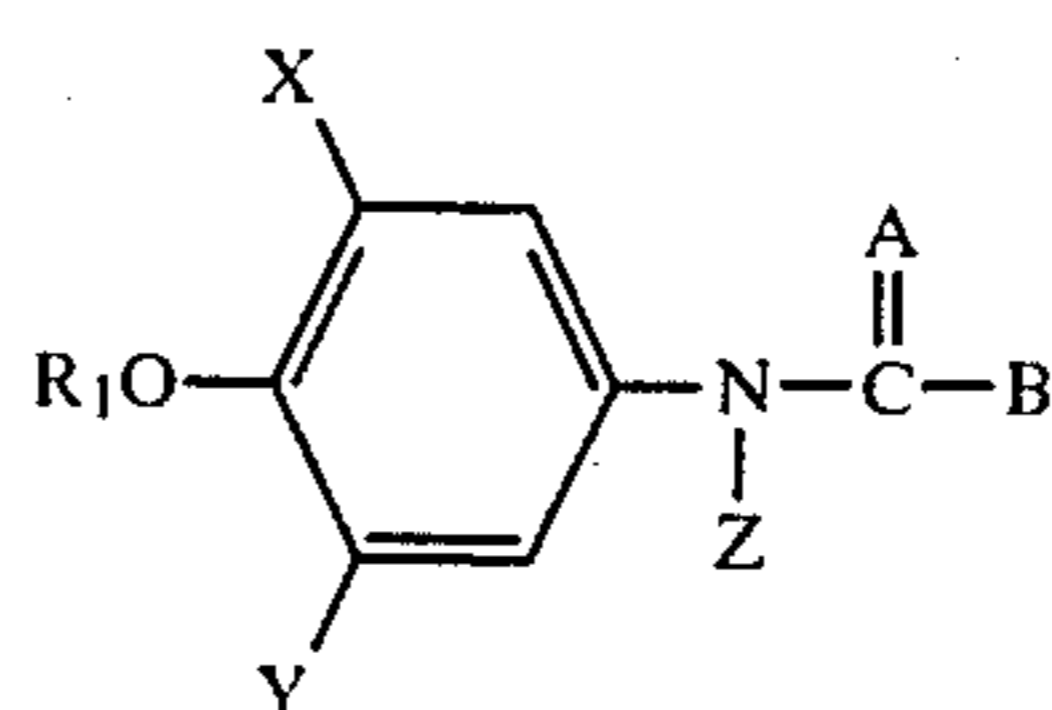
FUNGICIDAL ANILINE DERIVATIVES

This invention relates to fungicidal aniline derivatives.

Benzimidazole and thiophanate fungicides such as Benomyl (methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate), Fubelidazol (2-(2-furyl)benzimidazole), Thiabendazole (2-(4-thiazolyl)benzimidazole), Carben-dazim (methyl benzimidazol-2-ylcarbamate), Thiophanate-methyl (1,2-bis(3-methoxycarbonyl-2-thioureido)-benzene), Thiophanate (1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene), 2-(O,S-dimethylphosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene and 2-(O,O-dimethylthiophosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene are known to show an excellent fungicidal activity against various plant pathogenic fungi, and they have been widely used as agricultural fungicides since 1970. However, their continuous application over a long period of time provides phytopathogenic fungi with tolerance to them, whereby their plant disease-preventive effect is much lowered. Further, the fungi which have gained tolerance to certain kinds of benzimidazole or thiophanate fungicides also show considerable tolerance to some other kinds of benzimidazole or thiophanate fungicides. Thus, they are apt to obtain cross-tolerance. Therefore, if any material decrease of their plant disease-preventive effect in certain fields is observed, their application to such fields has to be discontinued. But, it is often observed that the density of drug-resistant organisms is not decreased even long after the application thereof has been discontinued. Although other kinds of fungicides have to be employed in such case, only few are so effective as benzimidazole or thiophanate fungicides in controlling various phytopathogenic fungi. Cyclic imide fungicides such as Procymidone (3-(3',5'-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide), Iprodione (3-(3',5'-dichlorophenyl)-1-isopropylcarbamoylimidazolidine-2,4-dione), Vinchlozolin (3-(3',5'-dichlorophenyl)-5-methyl-5-vinylloxazolidin-2,4-dione), ethyl(RS)-3-(3',5'-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate, etc., which are effective against various plant diseases, particularly those caused by *Botrytis cinerea*, have the same defects as previously explained with respect to the benzimidazole or thiophanate fungicides.

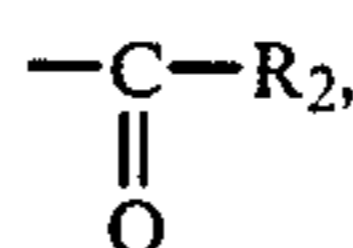
In C.R. Acad. Sc. Paris, t. 289, S'erie D, pages 691-693 (1979), it is described that such herbicides as Barban (4-chloro-2-butynyl N-(3-chlorophenyl)carbamate), Chlorobufam (1-methyl-2-propynyl N-(3-chlorophenyl)carbamate), Chlorpropham (isopropyl N-(3-chlorophenyl)carbamate) and Propham (isopropyl N-phenylcarbamate) exhibit a fungicidal activity against certain organisms tolerant to some of the benzimidazole or thiophanate fungicides. However, their fungicidal activity against the drug-resistant fungi is not strong enough, and hence, practically they can not be used as fungicides.

As a result of a study seeking a new type of fungicides, it has now been found that aniline derivatives of the formula:

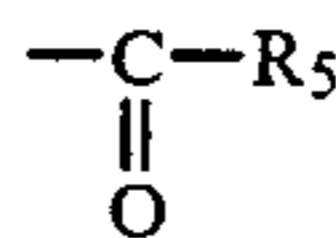


(I)

wherein X is fluoro(lower)alkyl group or a group of the formula:



—OR₃ or —CH₂R₄ in which R₂ is a lower alkenyl group, a lower alkynyl group, a cyano group or a lower alkylthio group, R₃ is a lower alkylcarbamoyl group, a lower alkenyl group, a lower alkynyl group, a cyano group, an acyl group, a lower alkoxy carbonyl group, a hydrogen atom or a lower alkyl group substituted with lower alkoxy, lower alkylthio, cyano or halogen and R₄ is an acyl group, a lower alkylthio group, a lower alkylcarbamoyloxy group or an acyloxy group; Y is a lower alkyl group, a lower alkoxy group, a halogen atom or a lower alkoxy methyl group; Z is a hydrogen atom, a hydroxyl group, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower alkoxy carbonyl(-lower)alkyl group or a group of the formula:



or —SR₆ in which R₅ is a lower alkyl group, a lower cyclo(lower)alkyl group or a phenyl group and R₆ is a lower alkyl group, a phenyl group or a lower alkoxy carbonyl group; R₁ is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a cyano group or a lower alkyl group substituted with halogen, lower alkoxy, cyano or cyclo(lower)alkyl; A is an oxygen atom or a sulfur atom; and B is a lower alkyl group, a lower alkenyl group, a cyclo(lower)alkyl group, a phenyl group or a group of the formula: —W—R₇ in which W is an oxygen atom or a sulfur atom and R₇ is a cyclo(lower)alkyl group, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a halo(lower)alkenyl group, a halo(lower)alkynyl group, a cyclo(lower)alkyl(lower)alkyl group or a lower alkyl group substituted with halogen, cyano, lower alkoxy, phenyl, lower alkenyloxy, halo(lower)alkoxy, phenoxy and/or ar(lower)alkoxy, show an excellent fungicidal activity against plant pathogenic fungi which have developed resistance to benzimidazole, thiophanate and/or cyclic imide fungicides. It is notable that their fungicidal potency against the organisms tolerant to benzimidazole, thiophanate and/or cyclic imide fungicides (hereinafter referred to as "drug-resistant fungi" or "drug-resistant strains") is much higher than that against the organisms sensitive to benzimidazole, thiophanate and/or cyclic imide fungicides (hereinafter referred to as "drug-sensitive fungi" or "drug-sensitive strains").

The term "lower" used hereinabove and hereinafter in connection with organic groups such as alkyl, alkenyl or alkynyl indicates groups having not more than 6 carbon atoms. Examples of the term "acyl" include lower alkanoyl and benzoyl.

The aniline derivatives of the formula (I) are fungicidally effective against a wide scope of plant pathogenic fungi, of which examples are as follows: *Podospaera leucotricha*, *Venturia inaequalis*, *Mycosphaerella pomi*, *Marssonina mali* and *Sclerotinia mali* of apple, *Phyllactinia kakicola* and *Gloeosporium kaki* of persimmon, *Cladosporium carpophilum* and *Phomopsis* sp. of peach, *Cercospora viticola*, *Uncinula necator*, *Elsinoe ampelina* and *Glomerella cingulata* of grape, *Cercospora beticola* of sugarbeet, *Cercospora arachidicola* and *Cercospora personata* of peanut, *Erysiphe graminis* f. sp. *hordei*, *Cercospora herpotrichoides* and *Fusarium nivale* of barley, *Erysiphe graminis* f. sp. *tritici* of wheat, *Sphaerotheca fuliginea* and *Cladosporium cucumerinum* of cucumber, *Cladosporium fulvum* of tomato, *Corynespora melongenae* of eggplant, *Sphaerotheca humuli*, *Fusarium oxysporum* f. sp. *fragariae* of strawberry, *Botrytis alli* of onion, *Cercospora apii* of celery, *Phaeoisariopsis griseola* of kidney bean, *Erysiphe cichoracearum* of tobacco, *Diplocarpon rosae* of rose, *Elsinoe fawcetti*, *Penicillium italicum*, *Penicillium digitatum* of orange, *Botrytis cinerea* of cucumber, eggplant, tomato, strawberry, pimiento, onion, lettuce, grape, orange, cyclamen, rose or hop, *Sclerotinia sclerotiorum* of cucumber, eggplant, pimiento, lettuce, celery, kidney bean, soybean, azuki bean, potato or sunflower, *Sclerotinia cinerea* of peach or cherry, *Mycosphaerella melonis* of cucumber or melon, etc. Namely, the compounds of the formula (I) are highly effective in controlling the drug-resistant strains of said fungi.

The compounds (I) are also fungicidally effective against fungi sensitive to said known fungicides as well as fungi to which said known fungicides are ineffective. Examples of such fungi are *Pyricularia oryzae*, *Pseudoperonospora cubensis*, *Plasmopara viticola*, *Phytophthora infestans*, etc.

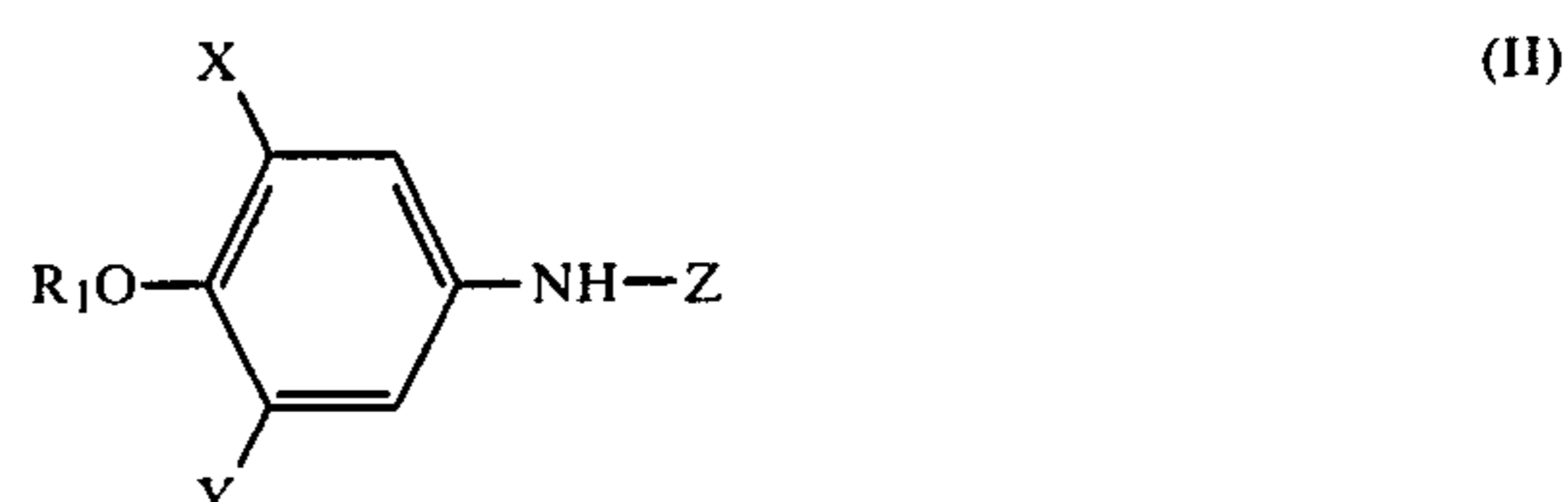
Advantageously, the compound (I) are of low toxicity and have little detrimental actions on mammals, fishes and so on. Also, they may be applied to an agricultural field without causing any material toxicity to important crop plants.

In view of their excellent fungicidal properties, preferred are the compounds (I) wherein X is a fluoromethyl group, a difluoromethyl group, a trifluoromethyl group, a methylthiocarbonyl group, an allyloxy group, a propargyloxy group, a methoxymethoxy group, a methylthiomethoxy group, a difluoromethoxy group or a 2-chloroethoxy group; Y is a methyl group, a methoxy group, an ethoxy group, a chlorine atom, a bromine atom or a methoxymethyl group; Z is a hydrogen atom; A is an oxygen atom; and B is a C₁-C₅ alkoxy group or a C₂-C₅ alkenyloxy group, a C₂-C₅ alkynyloxy group, a halo(C₁-C₅)alkyl group, a halo(C₂-C₅)alkenyloxy group, a halo(C₂-C₅)alkynyloxy group or a cyano(C₁-C₅)alkoxy group.

The aniline derivatives of the formula (I) can be prepared by either one of the following procedures:

Procedure (a)

The compound of the formula (I) can be prepared by reacting a compound of the formula:



wherein X, Y, Z and R₁ are each as defined above with a compound of the formula:



wherein A and B are each as defined above and R₈ is a halogen atom or with a compound of the formula:

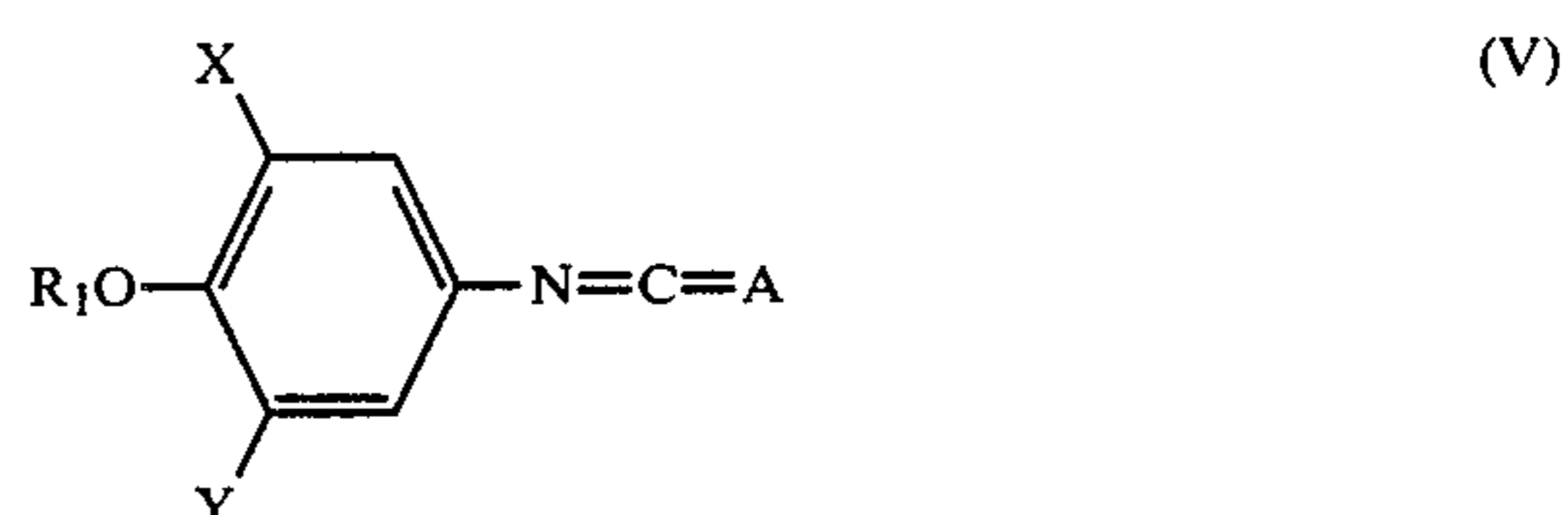


wherein A is as defined above and B' is a lower alkyl group, a lower alkenyl group, a cyclo(lower)alkyl group or a phenyl group.

The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, tetrahydrofuran, chloroform, ethyl acetate, dimethylformamide). If desired, the reaction may be performed in the presence of a base (e.g. triethylamine, sodium hydroxide, N,N-diethylaniline) so as to obtain the compound (I) in a high yield. The reaction may be accomplished at a temperature of 0° to 150° C. instantaneously or within 12 hours.

Procedure (b)

The compound of the formula (I) wherein Z is a hydrogen atom and B is a group of the formula: —W—R₇ in which W and R₇ are each as defined above can also be prepared by reacting a compound of the formula:



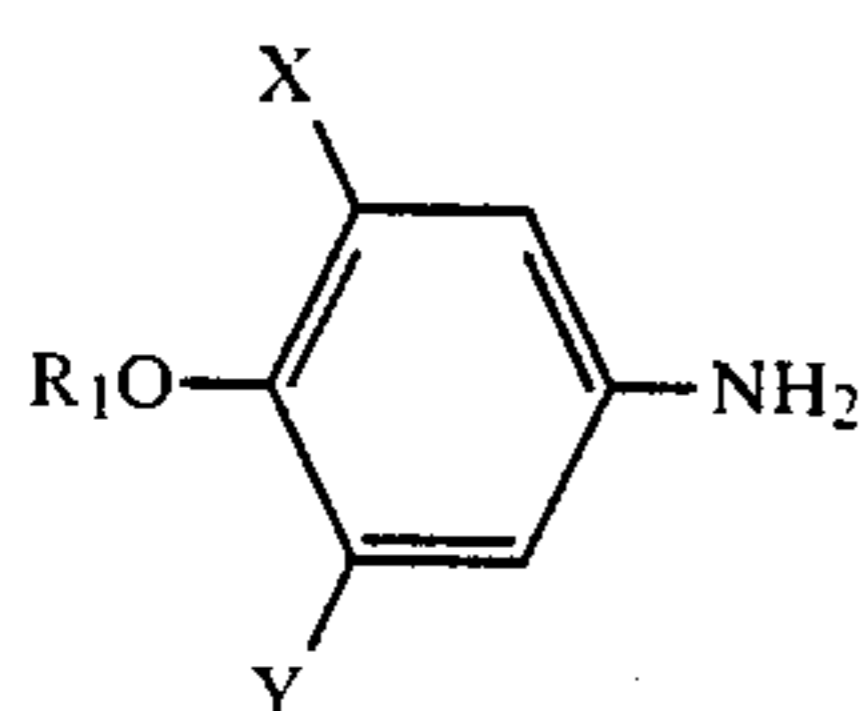
wherein X, Y, R₁ and A are each as defined above with a compound of the formula:



wherein W and R₇ are each as defined above.

The reaction is usually carried out in the absence or presence of an inert solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, dimethylformamide, chloroform, carbon tetrachloride). If desired, the reaction may be performed in the presence of a catalyst (e.g. triethylamine, N,N-diethylaniline, 1,4-diazabicyclo-[2.2.2]octane) as to obtain the compound (I) in a high yield. The reaction may be accomplished at a temperature of 0° to 50° C. instantaneously or within 10 hours.

The starting compound (V) can be prepared by reacting a compound of the formula:

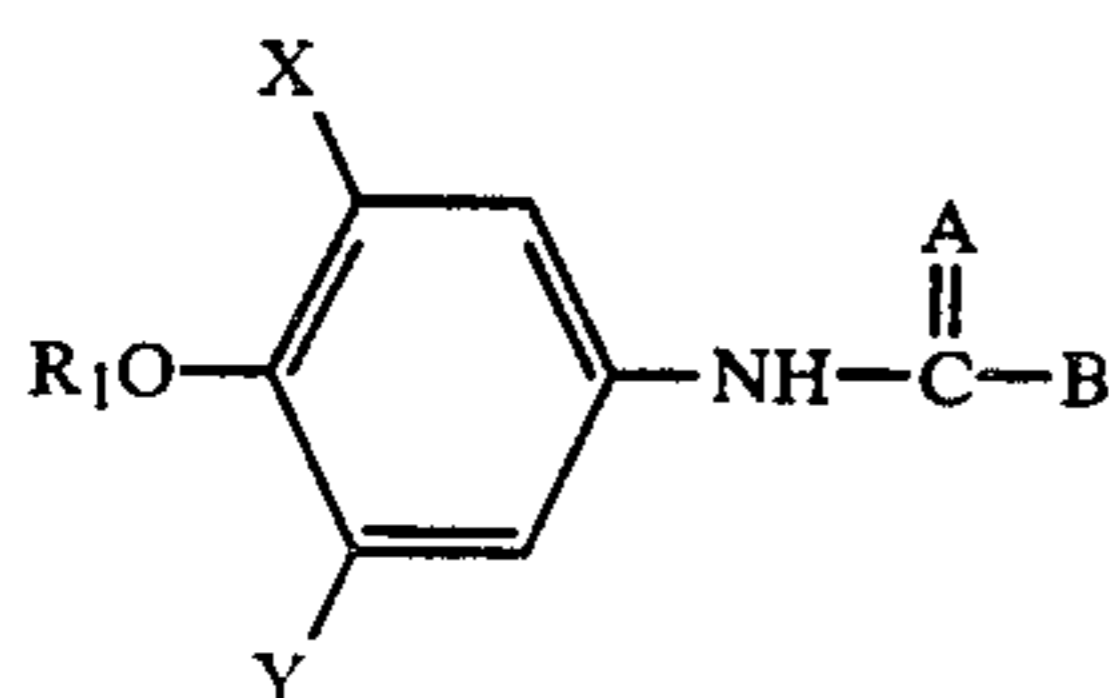


wherein X, Y and R₁ are each as defined above with phosgene or thiophosgene.

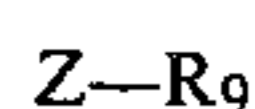
The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, xylene, ethyl acetate). The reaction may be accomplished at a temperature of 50° C. to the boiling point of the solvent instantaneously or within 10 hours.

Procedure (c)

The compound of the formula (I) can also be prepared by reacting a compound of the formula:



wherein X, Y, R₁, A and B are each as defined above with a compound of the formula:



wherein Z is as defined above and R₉ is a leaving group (e.g. tosyloxy, mesyloxy, halogen).

The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, xylene, dioxane, chloroform). If desired, a base (e.g. triethylamine, sodium hydroxide, sodium hydride) may be present in the reaction system. The reaction is normally accomplished at a temperature of 0° to 150° C. instantaneously or within 12 hours.

The compounds (II), (VII) and (VIII) in the above procedures are readily prepared by known methods.

Some typical examples for preparation of the compounds of the formula (I) are illustratively shown below.

EXAMPLE 1

Preparation of isopropyl

N-(3-acetyloxy-4,5-diethoxyphenyl)carbamate according to Procedure (a)

3-Acetyloxy-4,5-diethoxyaniline (1.0 g) and N,N-diethylaniline (0.70 g) were dissolved in toluene (15 ml). To the resultant solution was dropwise added isopropyl chloroformate (0.70 g) in 5 minutes under ice-cooling. The resultant mixture was allowed to stand at room temperature for 12 hours, poured into ice-water and extracted with ethyl acetate. The extract was washed

(VII)

with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using a mixture of benzene and tetrahydrofuran as the eluent to give isopropyl N-(3-acetyloxy-4,5-diethoxyphenyl)carbamate (Compound No. 4) (1.21 g) in a yield of 88.9%. M.P., 108°-109° C.

NMR (CDCl₃)δ: 1.25 (d, 6H), 1.30 (t, 3H), 1.38 (t, 3H), 2.27 (s, 3H), 3.96 (q, 2H), 4.00 (q, 2H), 4.95 (m, 1H), 6.46 (broad, 1H), 5.56 (d, 1H), 6.92 (d, 1H).

EXAMPLE 2

Preparation of 1-methyl-2-propynyl

N-[3-(2-chloroethoxy)-4-ethoxy-5-chlorophenyl]carbamate according to Procedure (b)

3-(2-Chloroethoxy)-4-ethoxy-5-chloroaniline (2.50 g) in toluene (20 ml) was dropwise added to a toluene solution containing 10 g of phosgene at 10° to 20° C. The resulting mixture was gradually heated and, after being refluxed for 30 minutes, cooled to room temperature. The solvent was removed by distillation under reduced pressure to give 3-(2-chloroethoxy)-4-ethoxy-5-chlorophenyl isocyanate. The thus obtained crude substance was added to a toluene solution (50 ml) containing triethylamine (1.0 g) and 1-butyne-3-ol (0.75 g). The resultant mixture was allowed to stand at room temperature for 12 hours, poured into ice-water and extracted with ethyl acetate. The extract was washed with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using a mixture of toluene and ethyl acetate as the eluent to give 1-methyl-2-propynyl N-[3-(2-chloroethoxy)-4-ethoxy-5-chlorophenyl]carbamate (Compound No. 31) (3.27 g) in a yield of 91.6%.

EXAMPLE 3

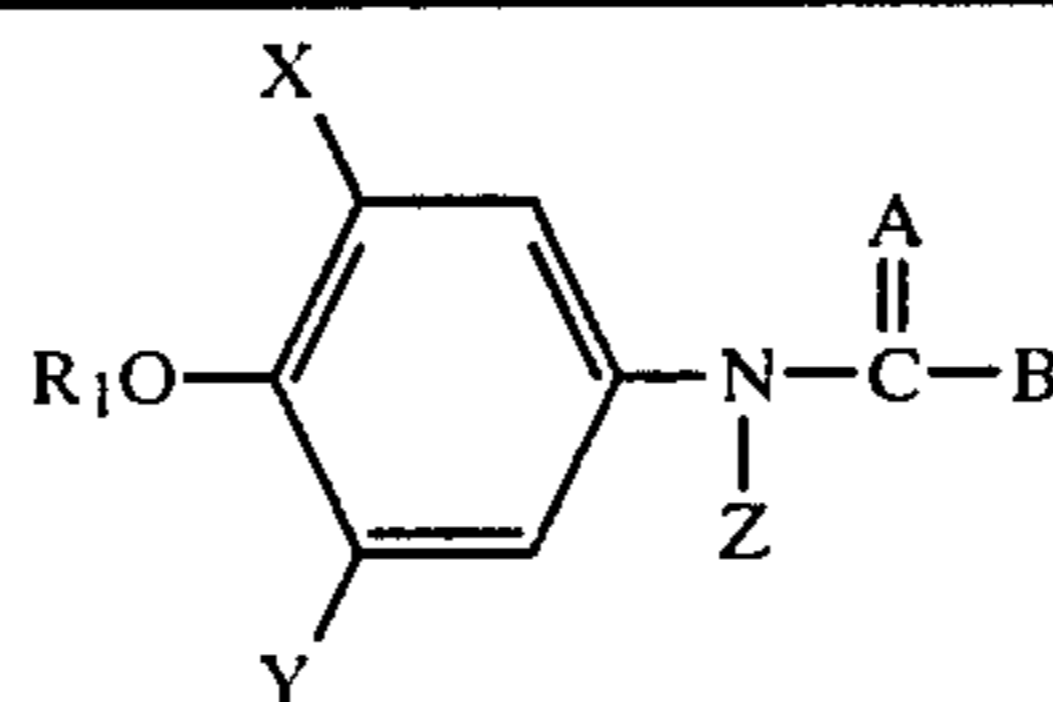
Preparation of isopropyl

N-methyl-N-(3,4-diethoxy-5-difluoromethoxyphenyl)carbamate according to Procedure (c)

Isopropyl N-(3,4-diethoxy-5-difluoromethoxyphenyl)carbamate (3.33 g) and iodomethane (4.30 g) were dissolved in tetrahydrofuran (10 ml). The resultant solution was dropwise added to a solution containing potassium hydroxide (1.68 g) and tetra-n-butylammonium bromide (1.0 g). After being allowed to stand at room temperature for 12 hours, the reaction mixture was poured into ice-water and extracted with toluene. The extract was washed with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using a mixture of toluene and ethyl acetate as the eluent to give isopropyl N-methyl-N-(3,4-diethoxy-5-difluoromethoxyphenyl)carbamate (Compound No. 55) (3.12 g) in a yield of 89.8%.

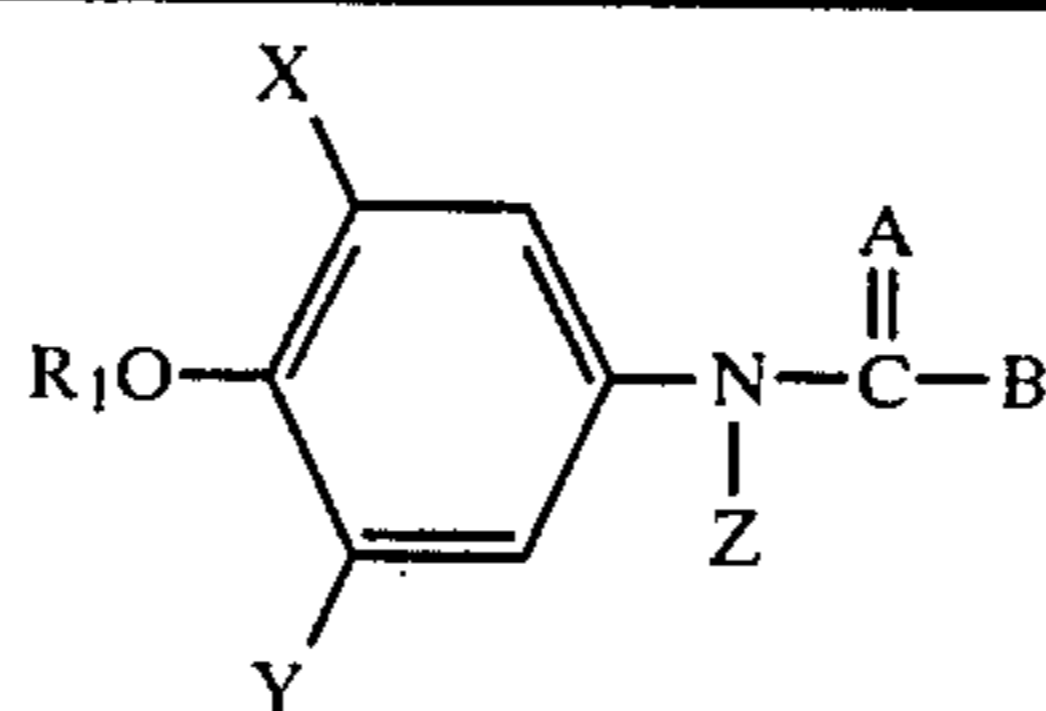
Specific examples of the compounds (I) of the present invention, which can be readily prepared according to Procedure (a), (b) or (c), are shown in Table 1.

TABLE I



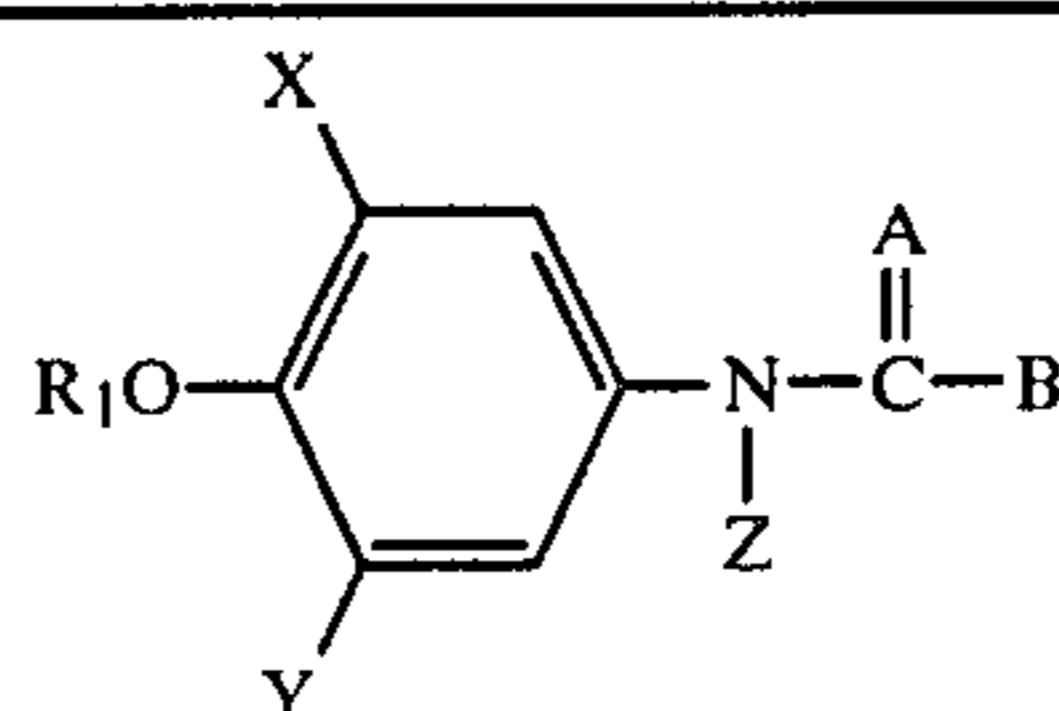
Compound No.	X	Y	R ₁	Z	A	B	Physical constant
1	$\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—SCH}_3$	$\text{—CH}_2\text{OCH}_3$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	$n_D^{28.5}$ 1.5319
2	$\text{—OCH}_2\text{CH=CH}_2$	$\text{—OC}_2\text{H}_5$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 117–118° C.
3	$\text{—OCH}_2\text{C}\equiv\text{CH}$	$\text{—OC}_2\text{H}_5$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 114–115° C.
4	$\text{—O—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—CH}_3$	$\text{—OC}_2\text{H}_5$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 108–109° C.
5	$\text{—O—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—OCH}_3$	$\text{—OC}_2\text{H}_5$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 79–80° C.
6	—OH	$\text{—OC}_2\text{H}_5$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 139–141° C.
7	$\text{—CH}_2\text{SCH}_3$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	$n_D^{26.0}$ 1.5481
8	$\text{—CH}_2\text{O—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—NH—CH}_3$	$\text{—CH}_2\text{OCH}_3$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	$n_D^{24.2}$ 1.5165
9	$\text{—CH}_2\text{O—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—CH}_3$	$\text{—CH}_2\text{OCH}_3$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	$n_D^{24.2}$ 1.5074
10	$\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—CH=CH}_2$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
11	$\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—C}\equiv\text{CH}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
12	$\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—C}\equiv\text{N}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 185–190° C.
13	$\text{—OC}\equiv\text{N}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 53–59° C.
14	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 75–78° C.
15	$\text{—CH}_2\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—CH}_3$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
16	$\text{—OCH}_2\text{C}\equiv\text{N}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 106–108° C.
17	$\text{—OCH}_2\text{OCH}_3$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	$n_D^{26.0}$ 1.5191
18	$\text{—OCH}_2\text{SCH}_3$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	NMR $\delta_{TMS}^{CDCl_3}$: 1.26(d,6H), 1.44(t,3H), 2.23(s,3H), 4.02(q,2H), 4.97(m,1H), 5.14(s,2H), 6.70(broad,1H), 6.99(d,1H), 7.03(d,1H).
19	$\text{—OCH}_2\text{CH}_2\text{F}$	—OCH_3	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 113.5–115° C.
20	$\text{—OCH}_2\text{CF}_3$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	$n_D^{24.5}$ 1.4821
21	$\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—SCH}_3$	—CH_3	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
22	—OCHF_2	$\text{—OC}_2\text{H}_5$	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	M.P. 81.5–84° C.
23	$\text{—CH}_2\text{SCH}_3$	—Br	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O(i)C}_3\text{H}_7$	

TABLE 1-continued



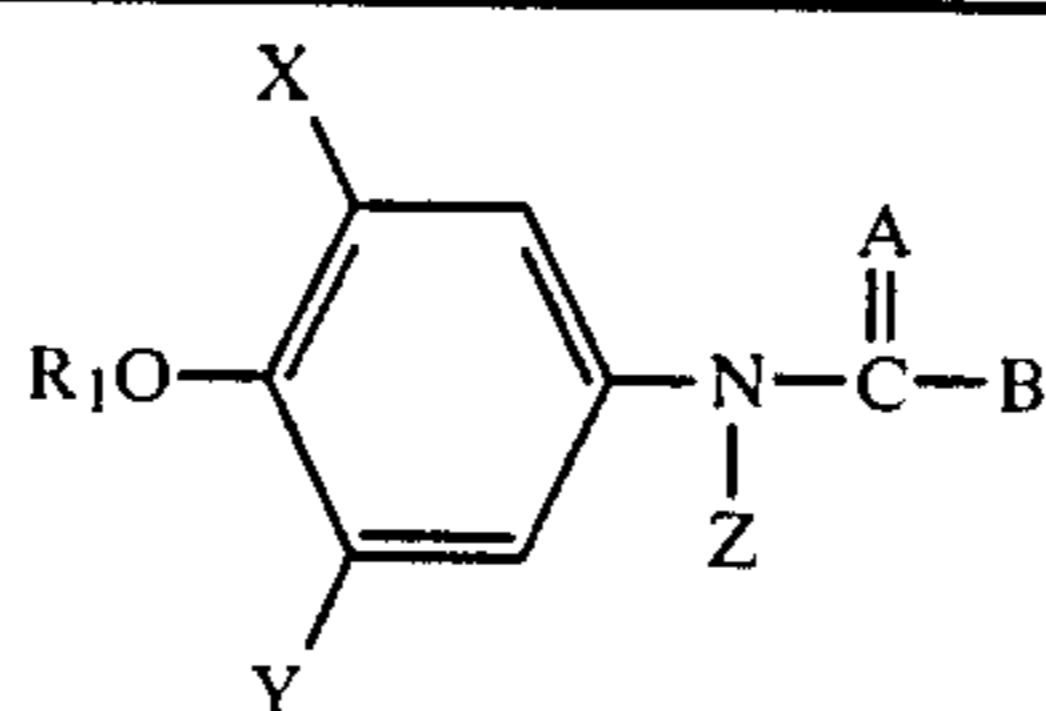
Compound No.	X	Y	R ₁	Z	A	B	Physical constant
24	—C—SCH_3 \parallel O	—CH_3	$\text{—CH}_2\text{CH=CH}_2$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
25	—C—SCH_3 \parallel O	—CH_3	$\text{—CH}_2\text{C}\equiv\text{CH}$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
26	—C—SCH_3 \parallel O	—CH_3	$\text{—CH}_2\text{CH}_2\text{F}$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
27	—C—SCH_3 \parallel O	—CH_3	$\text{—CH}_2\text{OCH}_3$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
28	—C—SCH_3 \parallel O	—CH_3	$\text{—CH}_2\text{C}\equiv\text{N}$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
29	—C—SCH_3 \parallel O	—CH_3	—CH_2	—H	O	$\text{—O(i)C}_3\text{H}_7$	
30	—C—SCH_3 \parallel O	—CH_3	$\text{—C}\equiv\text{N}$	—H	O	$\text{—O(i)C}_3\text{H}_7$	
31	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—O—CH—C}\equiv\text{CH}$ \mid CH_3	
32	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	—O—CH—CH=CH_2 \mid CH_3	
33	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	—O—CH—CH_3 \mid CH_2OCH_3	
34	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—OCH}_2\text{CH}_2\text{F}$	
35	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	—CH—CH_3 \mid C_2H_5	
36	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O		
37	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	—CH=CHCH_3	
38	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O		
39	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—OCH}_2\text{CH=CH}$ \mid CH_2Cl	
40	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—OCH}_2\text{C}\equiv\text{C}$ \mid CH_2Cl	
41	$\text{—OCH}_2\text{CH}_2\text{Cl}$	—Cl	$\text{—C}_2\text{H}_5$	—H	O	$\text{—OCH}_2\text{CH}_2\text{C}\equiv\text{N}$	

TABLE 1-continued



Compound No.	X	Y	R ₁	Z	A	B	Physical constant
42	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
43	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
44	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
45	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
46	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
47	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
48	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
49	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
50	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-H	O		
51	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-H	O	-SC ₂ H ₅	$n_D^{25.0}$ 1.5291
52	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-H	S	-OCH ₃	M.P. 92.5-93° C.
53	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-H	S	-SCH ₃	M.P. 121-123° C.
54	-OCH ₂ CH ₂ Cl	-Cl	-C ₂ H ₅	-OH	O	-O(i)C ₃ H ₇	
55	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-CH ₃	O	-O(i)C ₃ H ₇	$n_D^{25.0}$ 1.4842
56	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-CH ₂ CH=CH ₂	O	-O(i)C ₃ H ₇	$n_D^{25.0}$ 1.4825
57	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-CH ₂ C≡CH	O	-O(i)C ₃ H ₇	$n_D^{25.0}$ 1.4881
58	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅		O	-O(i)C ₃ H ₇	M.P. 90-93° C.
59	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅		O	-O(i)C ₃ H ₇	M.P. 47-49° C.
60		-OC ₂ H ₅	-C ₂ H ₅	-H	O	-O(i)C ₃ H ₇	M.P. 165-166° C.
61	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅		O	-O(i)C ₃ H ₇	M.P. 91-94° C.
62	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-CH ₂ COOCH ₃	O	-O(i)C ₃ H ₇	$n_D^{23.0}$ 1.4752
63	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-SCH ₃	O	-O(i)C ₃ H ₇	
64	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅		O	-O(i)C ₃ H ₇	

TABLE 1-continued



Compound No.	X	Y	R ₁	Z	A	B	Physical constant
65	-OCHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-SCOOC ₂ H ₅	O	-O(i)C ₃ H ₇	<i>n</i> _D ^{23.0} 1.4956
66	-CF ₃	-OC ₂ H ₅	-C ₂ H ₅	-H	O	-O(i)C ₃ H ₇	
67	-CHF ₂	-OC ₂ H ₅	-C ₂ H ₅	-H	O	-O(i)C ₃ H ₇	
68	-CH ₂ F	-OC ₂ H ₅	-C ₂ H ₅	-H	O	-O(i)C ₃ H ₇	
69	-OCF ₃	-OC ₂ H ₅	-C ₂ H ₅	-H	O	-O(i)C ₃ H ₇	

In the practical usage of the compounds (I) as fungicides, they may be applied as such or in a formulation form such as dusts, wettable powders, oil sprays, emulsifiable concentrates, tablets, granules, fine granules, aerosols or flowables. Such formulation form can be formulated in a conventional manner by mixing at least one of the compounds (I) with an appropriate solid or liquid carrier(s) or diluent(s) and, if necessary, an appropriate adjuvant(s) (e.g. surfactants, adherents, dispersants, stabilizers) for improving the dispersibility and other properties of the active ingredient.

Examples of the solid carriers or diluents are botanical materials (e.g. flour, tobacco stalk powder, soybean powder, walnut-shell powder, vegetable powder, saw dust, bran, bark powder, cellulose powder, vegetable extract residue), fibrous materials (e.g. paper, corrugated cardboard, old rags), synthetic plastic powders, clays (e.g. kaolin, bentonite, fuller's earth), talcs, other inorganic materials (e.g. pyrophyllite, sericite, pumice, sulfur powder, active carbon) and chemical fertilizers (e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, urea, ammonium chloride).

Examples of the liquid carriers or diluents are water, alcohols (e.g. methanol, ethanol), ketones (e.g. acetone, methylethylketone), ethers (e.g. diethyl ether, dioxane, cellosolve, tetrahydrofuran), aromatic hydrocarbons (e.g. benzene, toluene, xylene, methyl naphthalene), aliphatic hydrocarbons (e.g. gasoline, kerosene, lamp oil), esters, nitriles, acid amides (e.g. dimethylformamide, dimethylacetamide), halogenated hydrocarbons (e.g. dichloroethane, carbon tetrachloride), etc.

Examples of the surfactants are alkyl sulfuric esters, alkyl sulfonates, alkylaryl sulfonates, polyethylene glycol ethers, polyhydric alcohol esters, etc. Examples of the adherents and dispersants may include casein, gelatin, starch powder, carboxymethyl cellulose, gum arabic, alginic acid, lignin, bentonite, molasses, polyvinyl alcohol, pine oil and agar. As the stabilizers, there may be used PAP (isopropyl acid phosphate mixture), tricresyl phosphate (TCP), tolu oil, epoxidized oil, various surfactants, various fatty acids and their esters, etc.

The foregoing formulations generally contain at least one of the compounds (I) in a concentration of about 1 to 95% by weight, preferably of 2.0 to 80% by weight. By using the formulations, the compounds (I) are generally applied in such amounts as 2 to 100 g per 10 are.

When only the drug-resistant strains of phytopathogenic fungi are present, the compounds (I) may be used alone. However, when the drug-sensitive strains are present together with the drug-resistant strains, their alternate use with benzimidazole, thiophanate and/or cyclic imide fungicides or their combined use with benzimidazole, thiophanate fungicides and/or cyclic imide fungicides is favorable. In such alternate or combined use, each active ingredient may be employed as such or in conventional agricultural formulation forms. In case of the combined use, the weight proportion of the compound (I) and the benzimidazole, thiophanate and/or cyclic imide fungicide may be from about 1:0.1 to 1:10.0.

Typical examples of the benzimidazole, thiophanate and cyclic imide fungicides as shown in Table 2.

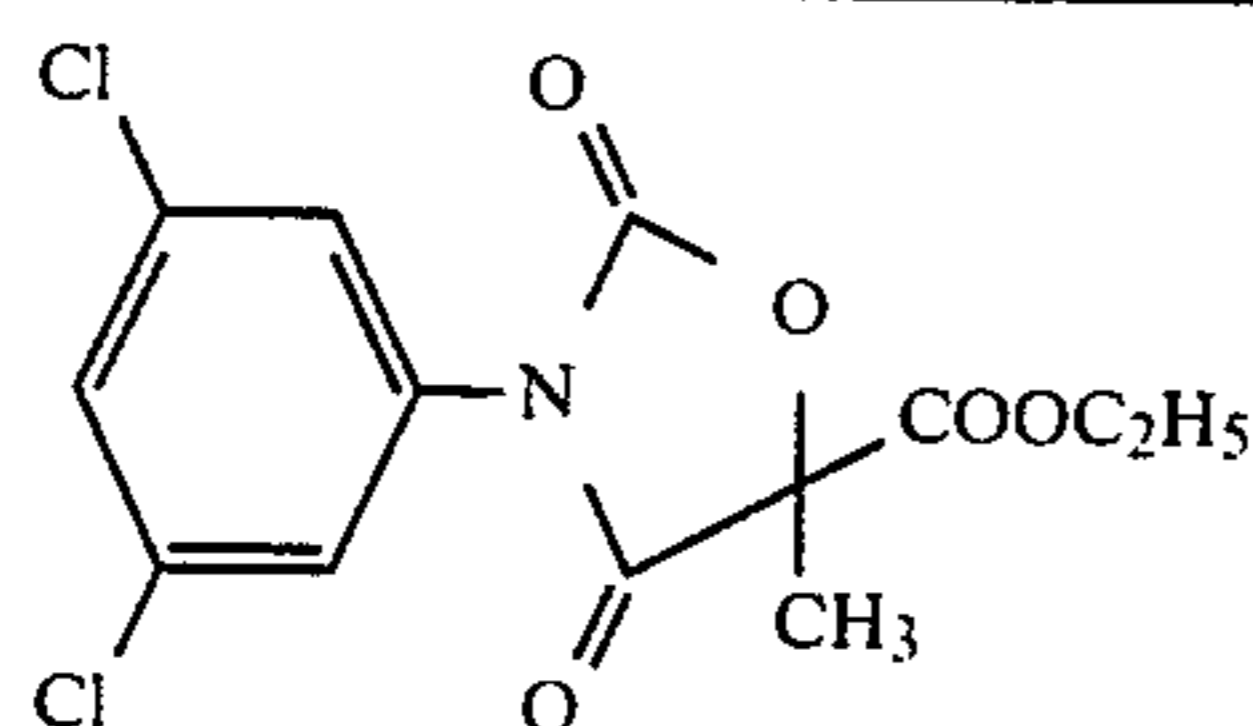
TABLE 2

Compound	Structure	Name
A		Methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate
B		2-(4-Thiazolyl)benzimidazole

TABLE 2-continued

Compound	Structure	Name
C		Methyl benzimidazol-2-ylcarbamate
D		2-(2-Furyl)benzimidazole
E		1,2-Bis(3-methoxycarbonyl-2-thio-ureido)benzene
F		1,2-Bis(3-ethoxycarbonyl-2-thio-ureido)benzene
G		2-(O,S-Dimethylphosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene
H		2-(O,O-Dimethylthiophosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene
I		N-(3',5'-Dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide
J		3-(3',5'-Dichlorophenyl)-1-isopropylcarbamoylimidazolidin-2,4-dione
K		3-(3',5'-Dichlorophenyl)-5-methyl-5-vinyloxazolidin-2,4-dione

TABLE 2-continued

Compound	Structure	Name
L		Ethyl (RS)-3-(3',5'-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate

Besides, the compounds (I) may be also used in admixture with other fungicides, herbicides, insecticides, miticides, fertilizers, etc.

When the compounds (I) are used as fungicides, they may be applied in such amounts as 2 to 100 grams per 10 ares. However, this amount may vary depending upon formulation forms, application times, application methods, application sites, diseases, crops and so on, and therefore, they are not limited to said particular amounts.

Some practical embodiments of the fungicidal composition according to the invention are illustratively shown in the following Examples wherein % are part(s) are by weight.

FORMULATION EXAMPLE 1

Two parts of Compound No. 1, 88 parts of clay and 10 parts of talc are thoroughly pulverized and mixed together to obtain a dust formulation containing 2% of the active ingredients.

FORMULATION EXAMPLE 2

Thirty parts of Compound No. 3, 45 parts of diatomaceous earth, 20 parts of white carbon, 3 parts of sodium laurylsulfate as a wetting agent and 2 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 30% of the active ingredients.

FORMULATION EXAMPLE 3

Fifty parts of Compound No. 17, 45 parts of diatomaceous earth, 2.5 parts of calcium alkylbenzenesulfonate as a wetting agent and 2.5 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 50% of the active ingredients.

FORMULATION EXAMPLE 4

Ten parts of Compound No. 14, 80 parts of cyclohexanone and 10 parts of polyoxyethylene alkylaryl ether as an emulsifier are mixed together to obtain an emulsifiable concentrate formulation containing 10% of the active ingredient.

FORMULATION EXAMPLE 5

One part of Compound No. 18, 1 part of Compound No. I, 88 parts of clay and 10 parts of talc are thoroughly pulverized and mixed together to obtain a dust formulation containing 2% of the active ingredient.

FORMULATION EXAMPLE 6

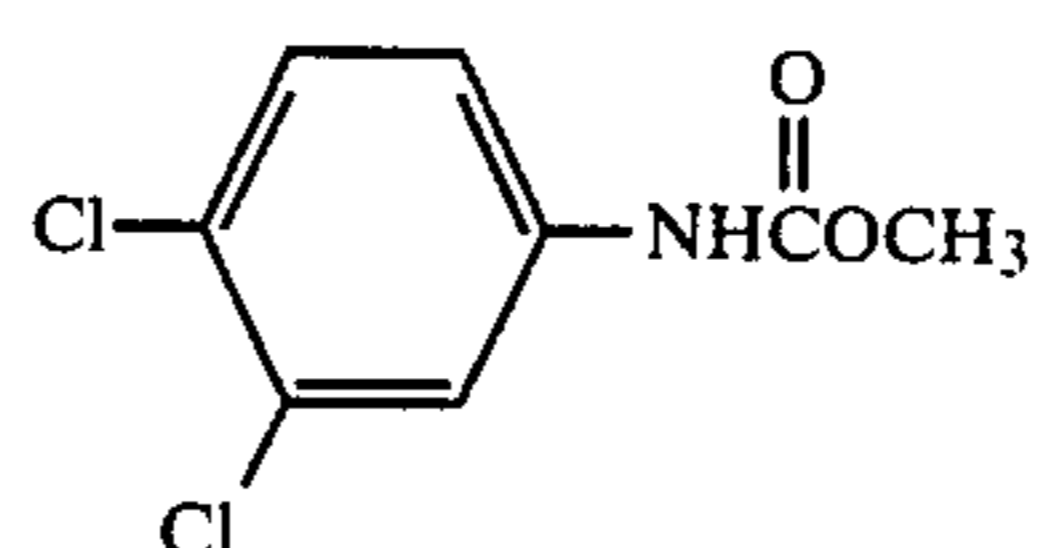
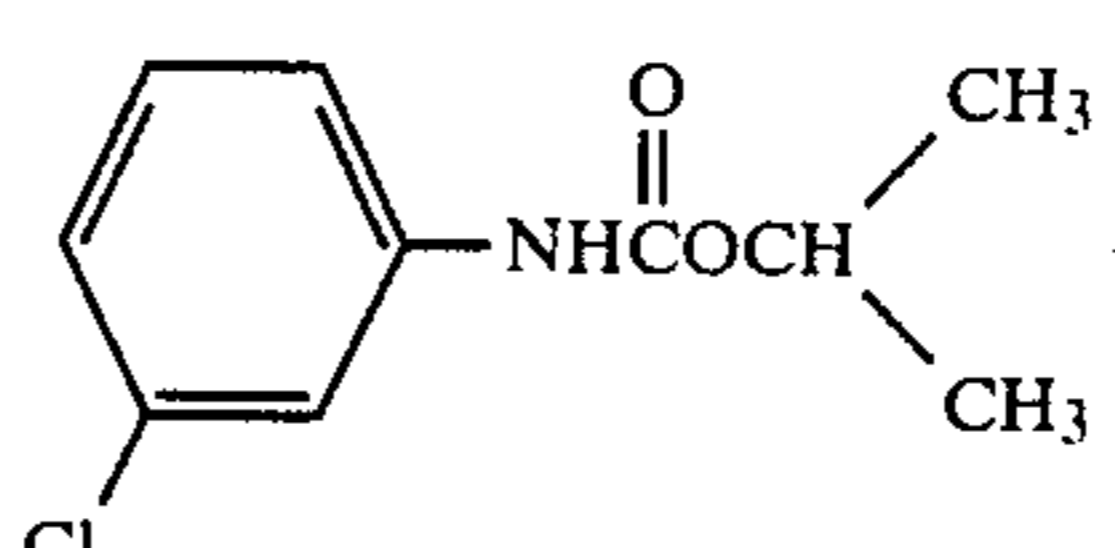
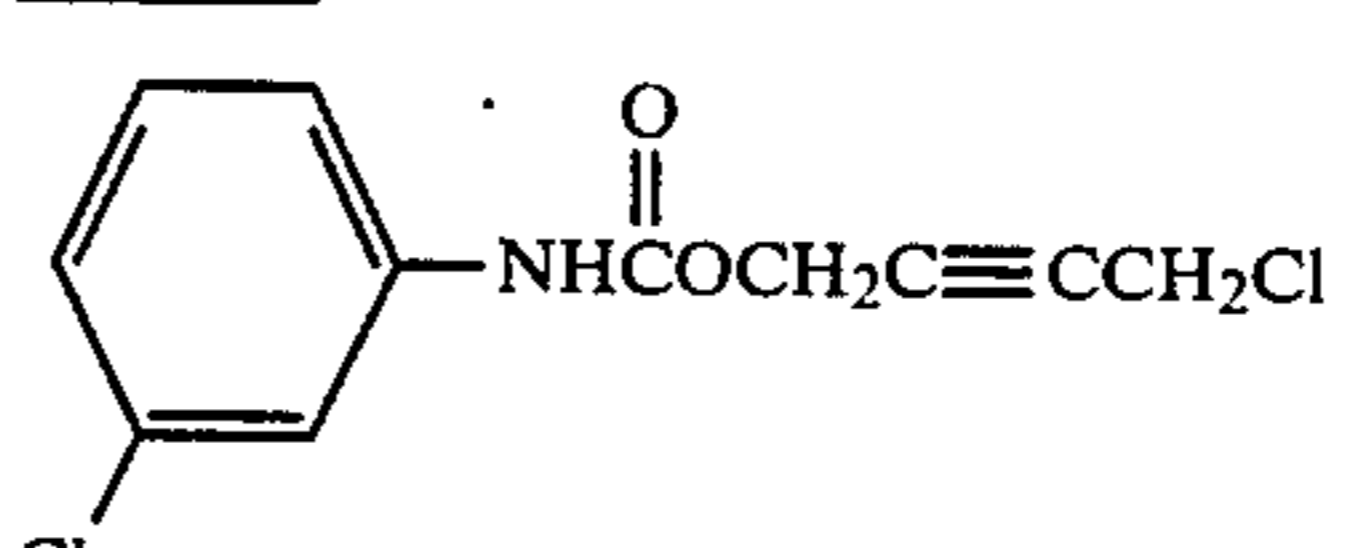
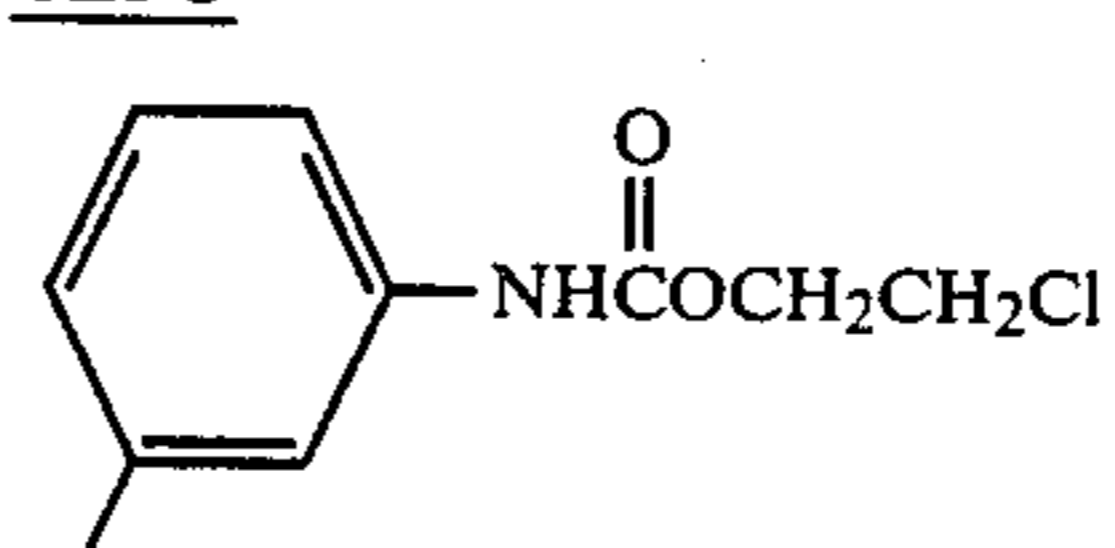
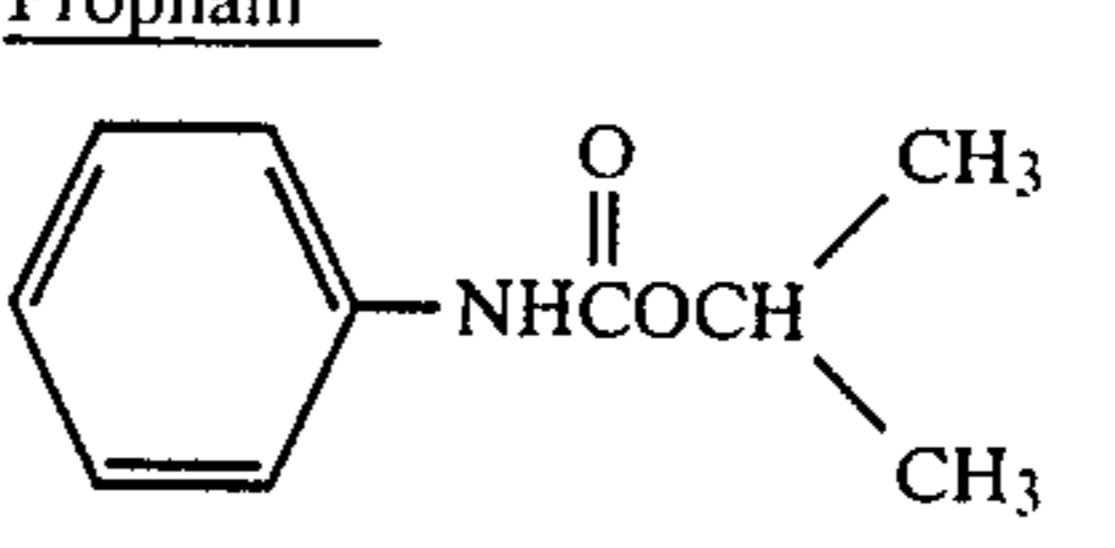
Twenty parts of Compound No. 5, 10 parts of Compound J, 45 parts of diatomaceous earth, 20 parts of white carbon, 3 parts of sodium laurylsulfate as a wetting agent and 2 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to

15 obtain a wettable powder formulation containing 30% of the active ingredients.

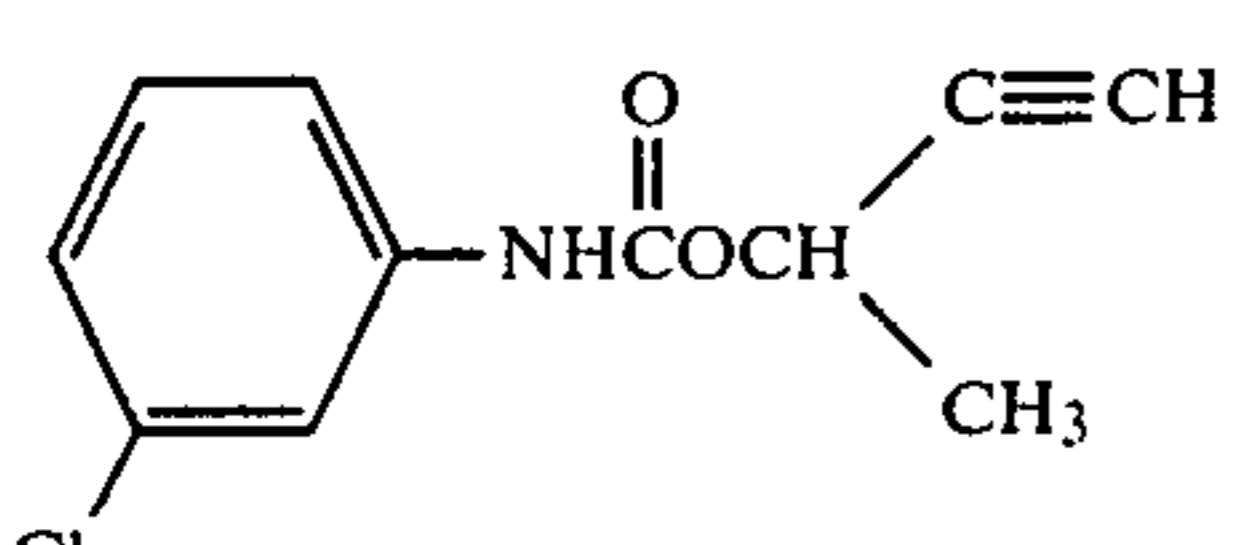
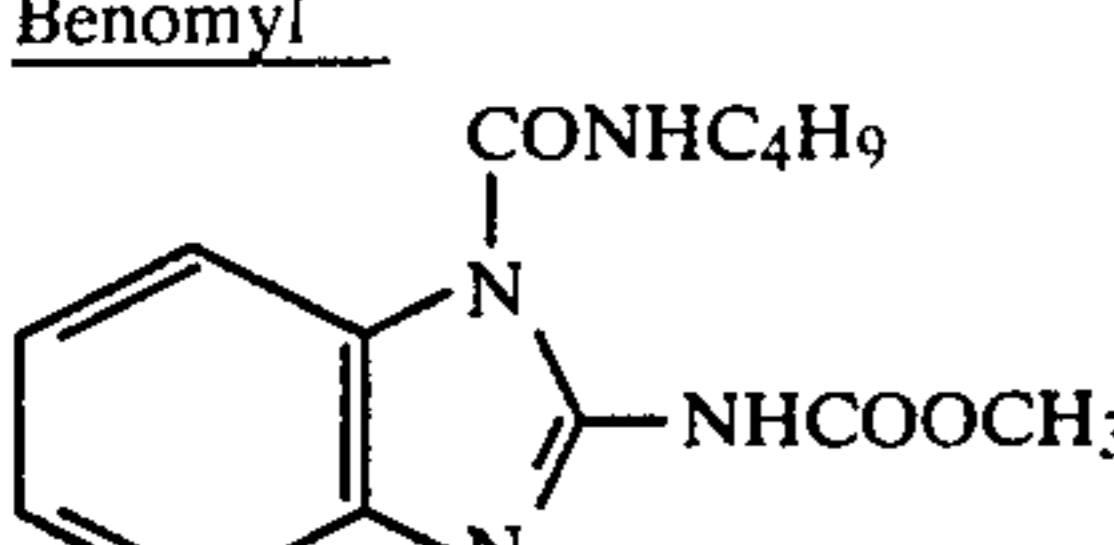
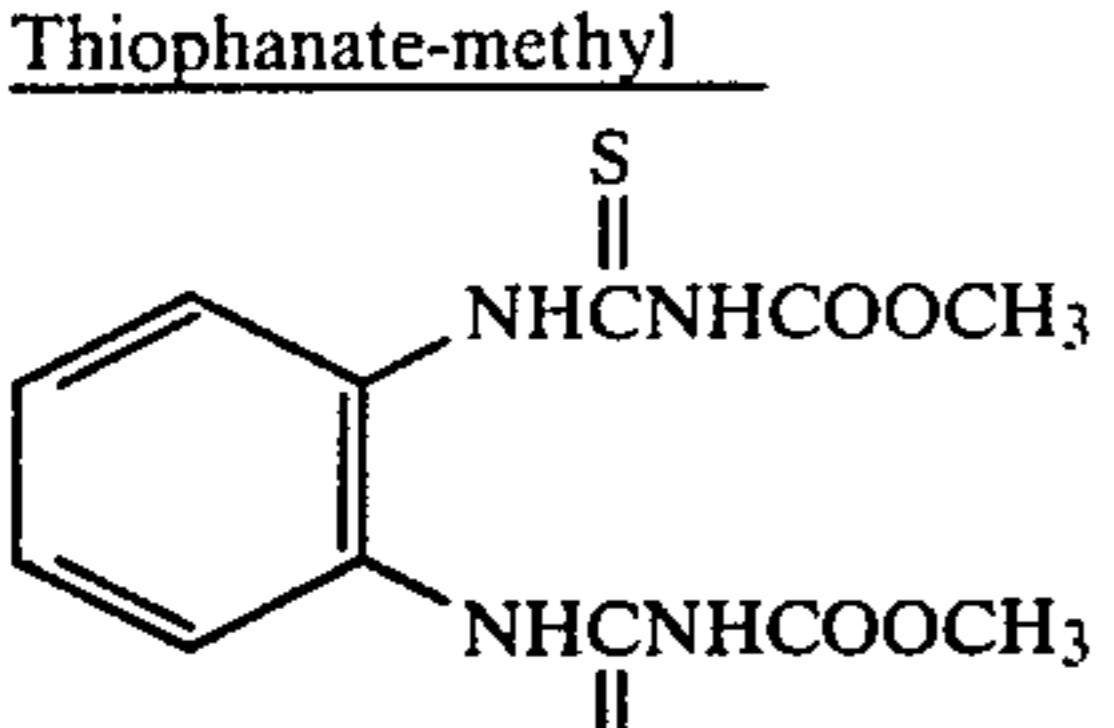
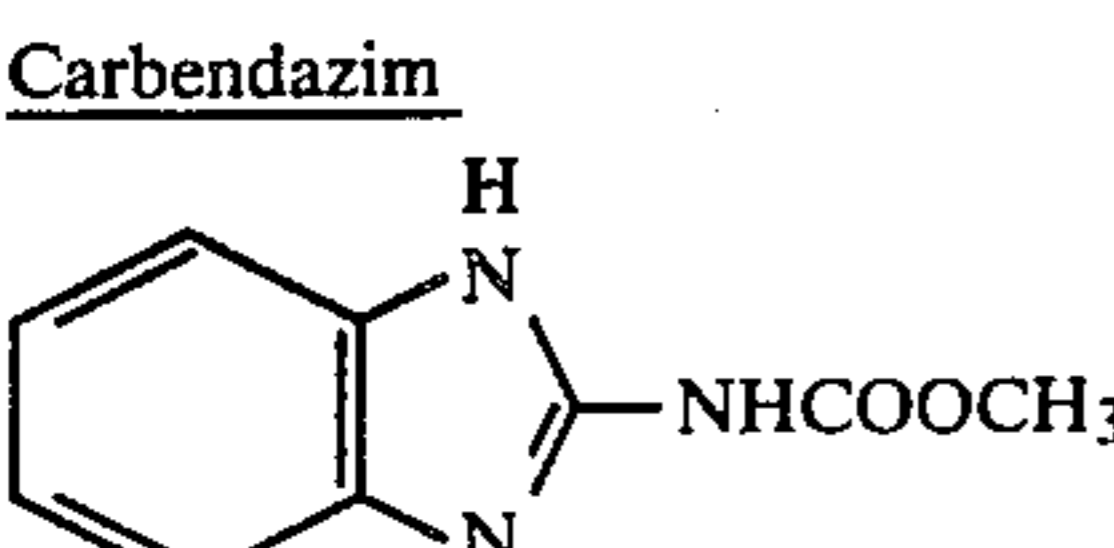
FORMULATION EXAMPLE 7

20 Ten parts of Compound No. 22, 40 parts of Compound A, 45 parts of diatomaceous earth, 2.5 parts of calcium alkylbenzenesulfonate as a wetting agent and 2.5 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 50% of the active ingredients.

25 Typical test data indicating the excellent fungicidal activity of the compounds of the formula (I) are shown below. The compounds used for comparison are as follows:

Compound	Remarks
30 <u>Swept</u>	
35 	Commercially available herbicide
40 <u>Chlorpropham</u>	
45 	Commercially available herbicide
<u>Barban</u>	
50 	Commercially available herbicide
<u>CEPC</u>	
55 	Commercially available herbicide
60 <u>Propham</u>	
65 	Commercially available herbicide
<u>Chlorbufam</u>	

-continued

Compound	Remarks
	Commercially available herbicide
<u>Benomyl</u> 	Commercially available fungicide
<u>Thiophanate-methyl</u> 	Commercially available fungicide
<u>Carbendazim</u> 	Commercially available fungicide

EXPERIMENT 1

Protective activity test on powdery mildew of cucumber (*Sphaerotheca fuliginea*)

A flower pot of 90 ml volume is filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) are sowed therein. Cultivation is carried out in a greenhouse for 8 days. Onto the resulting seedlings having cotyledons, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water is sprayed at a rate of 10 ml per pot. Then, the seedlings are inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Sphaerotheca fuliginea* by spraying and further cultivated in the greenhouse. Ten days thereafter, the infectious state of the plants is observed. The degree of damage is determined in the following manner, and the results are shown in Table 3.

The leaves examined are measured for a percentage of infected area and classified into the corresponding disease indices, 0, 0.5, 1, 2, 4:

Disease index	Percentage of infected area
0	No infection
0.5	Infected area of less than 5%
1	Infected area of less than 20%
2	Infected area of less than 50%
4	Infected area of not less than 50%

The disease severity is calculated according to the following equation:

Disease severity (%) =

-continued

$$\frac{\Sigma\{(\text{Disease index}) \times (\text{Number of leaves})\}}{4 \times (\text{Total number of leaves examined})} \times 100$$

The prevention value is calculated according to the following equation:

Prevention value (%) = 100 -

$$\frac{(\text{Disease severity in treated plot})}{(\text{Disease severity in untreated plot})} \times 100$$

TABLE 3

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	94	0
2	200	100	0
3	200	100	0
14	200	100	0
17	200	100	0
22	200	100	0
Swep	200	0	0
Chlorpropham	200	0	0
Barban	200	25	0
CEPC	200	0	0
Propham	200	0	0
Chlorbufam	200	0	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Carbendazim	200	0	100

As understood from the results shown in Table 3, the compounds (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl, Thiophanate-methyl and Carbendazim show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain. Other tested compounds structurally similar to the compounds (I) do not show any fungicidal activity on the drug-sensitive strain and the drug-resistant strain.

EXPERIMENT 2

Preventive effect on cercospora leaf spot of sugarbeet (*Cercospora beticola*)

A flower pot of 90 ml volume is filled with sandy soil, and seeds of sugarbeet (var: Detroit dark red) are sowed therein. Cultivation is carried out in a greenhouse for 20 days. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water is sprayed at a rate of 10 ml per pot. Then, the seedlings are inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Cercospora beticola* by spraying. The pot is covered with a polyvinyl chloride sheet to make a condition of high humidity, and cultivation is continued in the greenhouse for 10 days. The degree of damage is determined in the same manner as in Experiment 1, and the results are shown in Table 4.

TABLE 4

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
4	200	100	0
5	200	98	0
6	200	97	0
17	200	100	0
18	200	100	0
20	200	100	0
Swep	200	0	0
Chlorpropham	200	0	0
Barban	200	34	0
CEPC	200	0	0
Propham	200	0	0
Chlorbufam	200	0	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Carbendazim	200	0	100

As understood from the results shown in Table 4, the compounds (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl, Thiophanate-methyl and Carbendazim show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain. Other tested compounds structurally similar to the compounds (I) do not show any fungicidal activity on the drug-sensitive strain and the drug-resistant strain.

EXPERIMENT 3

Preventive effect on scab of pear (*Venturia nashicola*)

A plastic pot of 90 ml volume is filled with sandy soil, and seeds of pear (var: Chojuro) are sowed therein. Cultivation is carried out in a greenhouse for 20 days. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water is sprayed at a rate of 10 ml per pot. Then, the seedlings are inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Venturia nashicola* by spraying. The resulting plants are placed at 20° C. under a condition of high humidity for 3 days and then at 20° C. under irradiation with a fluorescent lamp for 20 days. The degree of damage is determined in the same manner as in Experiment 1, and the results are shown in Table 5.

TABLE 5

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
7	200	100	0
8	200	98	0
9	200	94	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 5, the compounds (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thioophanate-methyl

show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

EXPERIMENT 4

Preventive effect on brown leaf-spot of peanut (*Cercospora arachidicola*)

Plastic pots of 90 ml volume were filled with sandy soil, and seeds of peanut (var: Chiba hanryusei) were sowed therein. Cultivation was carried out in a greenhouse for 14 days. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Cercospora arachidicola* by spraying. The resulting plants were covered with a polyvinyl chloride sheet to make a condition of humidity and cultivated in the greenhouse for 10 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 6.

TABLE 6

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	100	0
4	200	100	0
5	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 6, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

EXPERIMENT 5

Preventive effect on gray mold of cucumber (*Botrytis cinerea*)

Plastic pots of 90 ml volume are filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) are sowed therein. Cultivation is carried out in a greenhouse for 8 days to obtain cucumber seedlings expanding cotyledons. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water is sprayed at a rate of 10 ml per pot. After air-drying, the seedlings were inoculated with mycelial disks (5 mm in diameter) of the drug-resistant or drug-sensitive strain of *Botrytis cinerea* by putting them on the leaf surfaces. After the plants are infected by incubating under high humidity at 20° C. for 3 days, the rates of disease severity are observed. The degree of damage is determined in the same manner as in Experiment 1, and the results are shown in Table 7.

TABLE 7

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	100	0
2	200	100	0
3	200	100	0
4	200	100	0
5	200	100	0
6	500	100	0
7	500	100	0
8	500	100	0
9	500	100	0
10	500	100	0
11	500	100	0
12	200	100	0
13	200	100	0
14	500	100	0
15	200	100	0
16	200	100	0
17	200	100	0
18	200	100	0
19	200	100	0
20	200	100	0
21	200	100	0
22	200	100	0
23	200	100	0
24	200	100	0
25	200	100	0
26	200	100	0
27	200	100	0
28	200	100	0
29	200	100	0
30	200	100	0
31	200	100	0
32	200	100	0
33	200	100	0
34	200	100	0
35	200	100	0
36	200	100	0
37	200	100	0
38	200	100	0
39	200	100	0
40	200	100	0
41	200	100	0
42	200	100	0
43	200	100	0
44	200	100	0
45	200	100	0
46	200	100	0
47	200	100	0
48	200	100	0
49	200	100	0
50	200	100	0
51	200	100	0
52	200	100	0
53	200	100	0
54	200	100	0
55	200	100	0
56	200	100	0
57	200	100	0
58	200	100	0
59	200	100	0
60	200	100	0
61	200	100	0
62	200	100	0
63	200	100	0
64	200	100	0
65	200	100	0
66	200	100	0
67	200	100	0
68	200	100	0
69	200	100	0
Benomyl	200	0	100
Thiophante-methyl	200	0	100

As understood from the results shown in Table 7, the compounds (I) of the invention show an excellent pre-

ventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

EXPERIMENT 6

Preventive effect on gummy stem blight of cucumber (*Mycosphaerella melonis*)

Plastic pots of 90 ml volume were filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days to obtain cucumber seedlings expanding cotyledons. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. After air-drying, the seedlings were inoculated with mycelial disks (5 mm in diameter) of the drug-resistant or drug-sensitive strain of *Mycosphaerella melonis* by putting them on the leaf surfaces. After the plants were infected by incubating under high humidity at 25° C. for 4 days, the rates of disease severity were observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 8.

TABLE 8

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
14	200	100	0
17	200	100	0
18	200	100	0
22	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 8, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

EXPERIMENT 7

Preventive effect on green mold of orange (*Penicillium italicum*)

Fruits of orange (var: Unshu) were washed with water and dried in the air. The fruits were immersed in a solution of the test compound prepared by diluting an emulsifiable concentrate comprising the test compound with water for 1 minute. After drying in the air, the fruits were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Penicillium italicum* by spraying and placed in a room of high humidity for 14 days. The degree of damage was determined in the following manner:

The fruits examined were measured for a percentage of infected area and classified into the corresponding indices, 0, 1, 2, 3, 4, 5:

Disease index	Percentage of infected area
0	No infection
1	Infected area of less than 20%
2	Infected area of less than 40%
3	Infected area of less than 60%
4	Infected area of less than 80%
5	Infected area of not less than 80%

Calculation of the degree of damage and the prevention value was made as in Experiment 1.

The results are shown in Table 9.

TABLE 9

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	100	0
33	200	100	0
34	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 9, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

EXPERIMENT 8

Phytotoxicity on crop plants

Plastic pots of 150 ml volume were filled with sandy soil, and seeds of wheat (var: Norin No. 61), apple (var: Kogyoku) and peanut (var: Chiba hanryusei) were sowed therein. Cultivation was carried out in a greenhouse. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed. After cultivation in the greenhouse for an additional 10 days, the phytotoxicity was examined on the following criteria:

Extent	Observation
—	No abnormality
+	Abnormality due to phytotoxicity observed in a part of crop plants
++	Abnormality due to phytotoxicity observed in entire crop plants
+++	Crop plants withered due to phytotoxicity

The results are shown in Table 10.

TABLE 10

Compound No.	Concentration of active ingredient (ppm)	Phytotoxicity		
		Wheat	Apple	Peanut
1	1000	—	—	—
17	1000	—	—	—
18	1000	—	—	—
Barban	1000	—	++	++
CEPC	1000	—	++	++

TABLE 10-continued

Compound No.	Concentration of active ingredient (ppm)	Phytotoxicity		
		Wheat	Apple	Peanut
Swep	1000	++	++	+

As understood from the results shown in Table 10, the compounds of the formula (I) of the invention produce no material phytotoxicity, while commercially available herbicides having a chemical structure similar thereto produce considerable phytotoxicity.

EXPERIMENT 9

Preventive effect on powdery mildew of cucumber (*Sphaerotheca fuliginea*)

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days. Onto the resulting seedlings having cotyledons, the test compound(s) formulated in an emulsifiable concentrate or wettable powder and diluted with water were sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a mixed spore suspension of the drug-resistant and drug-sensitive strain of *Sphaerotheca fuliginea* by spraying and further cultivated in the greenhouse. Ten days thereafter, the infectious state of the plants was observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 11.

TABLE 11

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
1	100	40
1	20	0
2	100	38
2	20	0
3	100	44
3	20	0
A	100	45
A	20	12
B	500	42
B	100	10
C	100	42
C	20	8
D	500	36
D	100	0
E	100	44
E	20	10
F	100	43
F	20	8
G	100	42
G	20	8
H	100	40
H	20	5
1 + A	20 + 20	100
1 + B	20 + 20	100
1 + E	20 + 20	100
1 + G	20 + 20	100
2 + C	20 + 20	100
2 + D	20 + 20	100
2 + F	20 + 20	100
2 + H	20 + 20	100
3 + A	20 + 20	100
3 + D	20 + 20	100
3 + E	20 + 20	100
3 + G	20 + 20	100

As understood from the results shown in Table 11, the combined use of the compounds of the formula (I) of the invention with benzimidazole, thiophanate and-

/or cyclic imide fungicides show much more excellent preventive effect than their sole use.

EXPERIMENT 10

Preventive effect on gray mold of tomato (*Botrytis cinerea*)

A plastic pot of 90 ml volume is filled with sandy soil, and seeds of tomato (var: Fukuju No. 2) are sowed therein. Cultivation is carried out in a greenhouse for 4 weeks. Onto the resulting seedlings at the 4-leaf stage, the test compound(s) formulated in an emulsifiable concentrate or wettable powder and diluted with water are sprayed at a rate of 10 ml per pot. Then, the seedlings are inoculated with a mixed spore suspension of the drug-resistant and drug-sensitive strain of *Botrytis cinerea* by spraying and placed at 20° C. in a room of high humidity for 5 days. The degree of damage is determined in the same manner as in Experiment 1, and the results are shown in Table 12.

TABLE 12

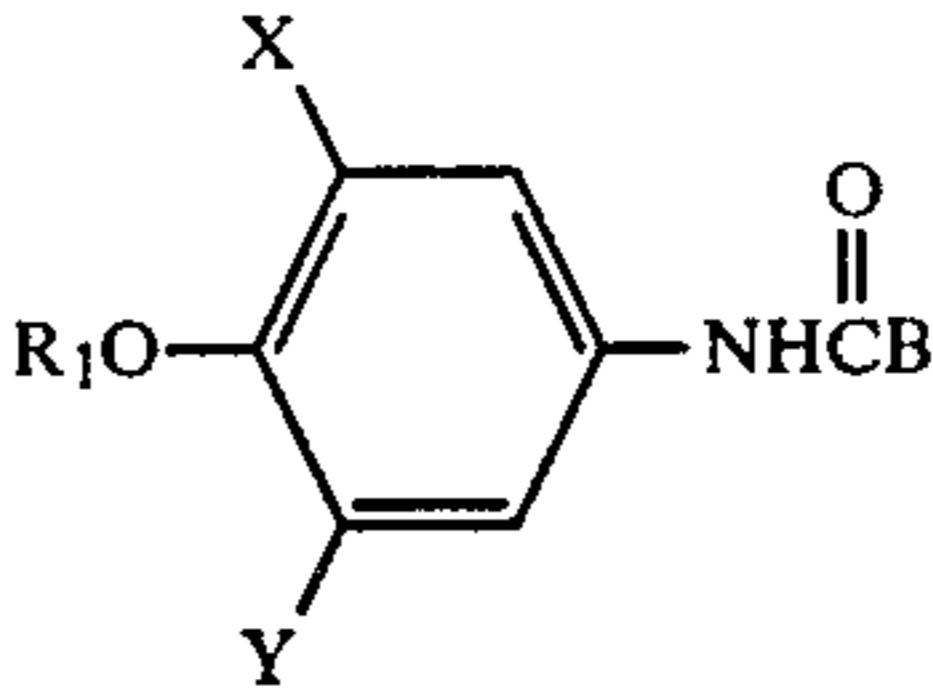
Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
4	100	40
4	20	0
5	100	38
5	20	0
9	100	42
9	20	0
I	100	48
I	20	22
J	500	46
J	100	18
K	100	42
K	20	15
L	500	42
L	100	12
4 + I	20 + 50	100
4 + J	20 + 50	100
5 + I	20 + 50	100

TABLE 12-continued

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
5 + K	20 + 50	100
9 + I	20 + 50	100
9 + J	20 + 50	100
9 + K	20 + 50	100
9 + L	20 + 50	100

As understood from the results shown in Table 12, the combined use of the compounds (I) of the invention with benzimidazole, thiophanate and/or cyclic imide fungicides show much more excellent preventive effect than their sole use.

What is claimed is:
1. A compound of the formula:



wherein X is a difluoromethoxy or 2-chloroethoxy group; Y is a methyl group, methoxy group, ethoxy group, chlorine, boromine or methoxymethyl group; B is a C₁-C₅ alkoxy group, a C₂-C₅ alkenyloxy group, a C₂-C₅ alkynyloxy group, a halo(C₁-C₅)alkyl group, a halo(C₂-C₅)alkenyloxy group, a halo(C₂-C₅)alkynyloxy group; and R₁ is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a cyano group or a lower alkyl group substituted with halogen, lower alkoxy, cyano or cyclo(lower)alkyl.

2. A fungicidal composition which comprises as an essential active ingredient a fungicidally effective amount of a compound according to claim 1, and an inert carrier or diluent.

3. The compound according to claim 1, wherein X is —OCH₂CH₂Cl, Y is chlorine, R₁ is ethyl, and B is an isopropoxy group.

* * * * *